

CLAIMS

Therefore, at least the following is claimed:

- 1 1. A membrane, comprising:
2 a flexible proton electrolyte membrane having the characteristic of a
3 proton conductivity of about 1×10^{-6} to 1×10^{-1} S/cm at a temperature range of
4 about 30°C to about 180°C and a relative humidity of about 0% to 100%.

- 1 2. A fuel cell, comprising:
2 a flexible proton electrolyte membrane having the characteristic of a
3 proton conductivity of about 1×10^{-6} to 1×10^{-1} S/cm at a temperature range of
4 about 30°C to about 180°C and a relative humidity of about 0% to 100%; with the
5 proviso that the fuel cell does not include a humidifier, a catalyst, and a thermal
6 management system for controlling the temperature in the fuel cell.

- 1 3. A flexible proton electrolyte membrane, comprising:
2 a hybrid inorganic-organic copolymer network having at least one
3 backbone unit having a formula $[-O-Si(WX)-O-Si(YZ)-R^1-]$, wherein each of W,
4 X, Y, and Z is selected from $-OPO_3H_2$, $-R^2A$, $-R^3$, $-O-$, and $-OPO_3H_2$, and
5 wherein R^1 , R^2 , and R^3 are each hydrocarbons.

- 1 4. The membrane of claim 3, wherein R^1 is selected from a linear C_2 to C_{20}
2 hydrocarbon, a branched C_2 to C_{20} hydrocarbon, a halogen-substituted linear C_2 to
3 C_{20} hydrocarbon, and a halogen-substituted branched C_2 to C_{20} hydrocarbon.
- 1 5. The membrane of claim 3, wherein R^2 is selected from a linear C_2 to C_{20}
2 hydrocarbon, a branched C_2 to C_{20} hydrocarbon, a hydrocarbon including an
3 aromatic ring, a halogen-substituted linear C_2 to C_{20} hydrocarbon, a halogen-
4 substituted branched C_2 to C_{20} hydrocarbon, and a halogen-substituted
5 hydrocarbon including an aromatic ring.
- 1 6. The membrane of claim 3, wherein R^3 is selected from CH_3 and C_2H_5 .
- 1 7. The membrane of claim 3, wherein A is selected from $-SO_3H$, $SO_2NHSO_2CF_3$,
2 $-CF_2SO_3H$, and $-CF_2SO_2NHSO_2CF_3$.
- 1 8. The membrane of claim 3, wherein the backbone unit is crosslinked with a second
2 backbone unit.
- 1 9. The membrane of claim 3, wherein each of W, X, Y, and Z are different.
- 1 10. The membrane of claim 3, wherein the backbone unit has a formula
2 $[-O-Si(WX)-O-Si(YZ)-R^1-O-R^4]$, wherein each of W, X, Y, and Z is selected
3 from, $-R^2A$, $-R^3$, $-O-$, and $-OPO_3H_2$, wherein R^4 is a hydrocarbon.

- 1 11. The membrane of claim 10, wherein R^4 is selected from a linear C_2 to C_{20}
2 hydrocarbon, a branched C_2 to C_{20} hydrocarbon, a halogen-substituted linear C_2 to
3 C_{20} hydrocarbon, and a halogen-substituted branched C_2 to C_{20} hydrocarbon.
- 1 12. The membrane of claim 3, wherein the backbone unit has a formula
2 $[-O-Si(WX)-O-Si(YQ)-R^1-Si(YQ)-]$, wherein each of W, X, and Y is selected
3 from $-OPO_3H_2$, $-R^2A$, $-R^3$, $-OPO_3H_2$, wherein Q includes $-O-Si-R^8-Si-$ wherein R^2
4 and R^3 are each hydrocarbons, wherein each of R^1 and R^8 are selected from a short
5 chain hydrocarbon and a long chain hydrocarbon, wherein R^1 and R^8 are different,
6 wherein the short chain hydrocarbon is selected from a linear C_2 to C_{20}
7 hydrocarbon, a branched C_2 to C_{20} hydrocarbon, a halogen-substituted linear C_2 to
8 C_{20} hydrocarbon, and a halogen-substituted branched C_2 to C_{20} hydrocarbon, and
9 wherein a long chain hydrocarbon is selected from a hydrocarbon having a
10 molecular weight from about 500 to 100,000 and a halogen-substituted
11 hydrocarbon having a molecular weight from about 500 to 100,000.
- 1 13. The membrane of claim 3, wherein the membrane is incorporated in a fuel cell.

- 1 14. A membrane formed from mixing components comprising:
2 at least one hybrid inorganic-organic copolymer network former
3 compound;
4 a first compound including an inorganic acid group;
5 a Si-O-Si inorganic backbone former compound; and
6 a H₃PO₄ compound.
- 1 15. The membrane of claim 14, wherein the inorganic acid group is selected from
2 -SO₃H, -SO₂NHSO₂CF₃, -CF₂SO₃H, and -CF₂SO₂NHSO₂CF₃.
- 1 16. The membrane of claim 14, wherein the hybrid inorganic-organic copolymer
2 network former compound includes an epoxide ring containing alkoxysilane
3 compound.
- 1 17. The membrane of claim 16, wherein the epoxide ring containing alkoxysilane
2 compound is selected from an aliphatic epoxide ring containing alkoxysilane
3 compound and a cycloaliphatic epoxide ring containing alkoxysilane compound.
- 1 18. The membrane of claim 17, wherein the epoxide ring containing alkoxysilane
2 compound is selected from (D_{3-x}M_x)SiR⁵C₂H₃O and (D_{3-x}M_x)SiR⁵C₆H₉O, wherein
3 D can be selected from C₂H₅O and CH₃O, M is selected from C₂H₅ and CH₃, R⁵ is
4 a C₂ to C₂₀ hydrocarbon chain, and x is from 0 to 2.

- 1 19. The membrane of claim 17, wherein the epoxide ring containing alkoxysilane
2 compound is selected from (3-glycidoxypropyl)methyldiethoxysilane, (3-
3 glycidoxypropyl)methyldimethoxysilane, (3-glycidoxypropyl)triethoxysilane, (3-
4 glycidoxypropyl)trimethoxysilane, 5,6-epoxyhexyltriethoxysilane, 5,6-
5 epoxyhexyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, and 2-
6 (3,4-epoxycyclohexyl)ethyltrimethoxysilane.
- 1 20. The membrane of claim 14, wherein the hybrid inorganic-organic copolymer
2 network former is selected from an aliphatic diepoxide monomer and a
3 cycloaliphatic diepoxide monomer.
- 1 21. The membrane of claim 20, wherein the hybrid inorganic-organic copolymer
2 network former is selected from $(\text{C}_2\text{H}_3\text{O})\text{R}^6(\text{C}_2\text{H}_3\text{O})$ and $\text{C}_6\text{H}_9\text{OR}^6\text{C}_6\text{H}_9\text{O}$,
3 wherein R is a C_2 to C_{20} hydrocarbon chain.
- 1 22. The membrane of claim 20, wherein the hybrid inorganic-organic copolymer
2 network former is selected from 1,3-butadiene diepoxide, dicyclopentadiene
3 diepoxide, and 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexanecarboxylate.

1 23. The membrane of claim 14, wherein first compound including an inorganic acid
2 group includes $(D_{3-x}M_x)SiR^7A$, wherein D can be selected from C_2H_5O and CH_3O ,
3 M is selected from C_2H_5 and CH_3 , R^7 is a C_2 to C_{20} hydrocarbon chain, x is from 0
4 to 2, and wherein A is an inorganic acid group is selected from $-SO_3H$, -
5 $SO_2NHSO_2CF_3$, $-CF_2SO_3H$, and $-CF_2SO_2NHSO_2CF_3$.

1 24. The membrane of claim 14, wherein the first compound including an inorganic
2 acid group is selected from sulfonated phenyltriethoxysilane (SPS), sulfonated
3 phenylethyltriethoxysilane, and 3-(trihydroxysilyl)-1-propane sulfonic acid.

1 25. The membrane of claim 14, wherein the Si-O-Si inorganic backbone former
2 compound is selected from tetraethoxysilane and tetramethoxysilane.

1 26. The membrane of claim 14, wherein the hybrid inorganic-organic copolymer
2 network former compound is from about 20 to 80 mole ratio of the membrane, the
3 first compound including an inorganic acid functional group is from about 0 to 20
4 mole ratio of the membrane, the Si-O-Si inorganic backbone former compound is
5 from about 20 to 80 mole ratio of the membrane, and the H_3PO_4 compound is
6 about 0.1 to 1.5 times the total Si moles in the membrane.

- 1 27. A membrane formed from mixing components comprising:
- 2 a bis(alkylalkoxysilyl)-terminated polymer compound;
- 3 a bis(trialkoxysilyl)-terminated short organic chain compound;
- 4 a first compound including an inorganic acid group;
- 5 a Si-O-Si inorganic backbone former compound; and
- 6 a H₃PO₄ compound.
- 1 28. The membrane of claim 27, further comprising a heterocycle compound.
- 1 29. The membrane of claim 28, wherein the imidazole-ring containing compound is
- 2 selected from imidazole, benzimidazole, 2-phenyl imidazole (PI), 2-methyl 4-
- 3 ethyl imidazole, and imidazole-2-carboxaldehyde.
- 1 30. The membrane of claim 27, wherein the bis(alkylalkoxysilyl)-terminated polymer
- 2 compound includes (D_{3-x}M_x)SiR⁹Si (D_{3-x}M_x), wherein D can be selected from
- 3 C₂H₅O and CH₃O, M is selected from C₂H₅ and CH₃, R⁹ is a linear C₂ to C₂₀
- 4 hydrocarbon chain, and x is from 1 to 2.

1 31. The membrane of claim 30, wherein the bis(alkylalkoxysilyl)-terminated polymer
 2 compound is selected from bis((3-methyldimethoxysilyl)propyl)polypropylene
 3 oxide, bis((3-methyldimethoxysilyl)propyl)polytetraethylene oxide,
 4 bis(methyldimethoxysilyl)poly(1-butene), bis(methyldimethoxysilyl)polyethylene,
 5 bis(dimethylmethoxysilyl)polyethylene, bis(methyldimethoxysilyl)polypropylene,
 6 bis(methyldimethoxysilyl)polyvinylidene fluoride,
 7 bis(methyldimethoxysilyl)polystyrene,
 8 bis(methyldimethoxysilyl)polytetrafluoroethylene,
 9 bis(methyldimethoxysilyl)polyvinyl chloride, and
 10 bis(methyldimethoxysilyl)polyvinyl alcohol.

1 32. The membrane of claim 27, wherein the bis(trialkoxysilyl)-terminated short organic
 2 chain compound includes $(D_3)SiR^{10}Si(D_3)$, wherein D can be selected from C_2H_5O
 3 and CH_3O , R^{10} is a linear C_2 to C_{20} hydrocarbon chain, and x is from 1 to 2.

1 33. The membrane of claim 32, wherein the bis(alkylalkoxysilyl)-terminated polymer
 2 compound is selected from bis(triethoxysilyl)ethane, bis(triethoxysilyl)octane,
 3 bis(triethoxysilyl)nonane, bis(triethoxysilyl)methane,
 4 bis(triethoxysilylethyl)benzene, bis(triethoxysilyl)hexane,
 5 bis(trimethoxysilylpropyl)amine, bis[(trimethoxysilyl)propyl]ethylenediamine,
 6 bis(trimethoxysilyl)ethane, bis(trimethoxysilyl)octane, bis(trimethoxysilyl)nonane,
 7 bis(trimethoxysilyl)methane, bis(trimethoxysilylethyl)benzene, and
 8 bis(trimethoxysilyl)hexane.

- 1 34. The membrane of claim 27, wherein the first compound including an inorganic acid
2 group includes $(D_{3-x}M_x)SiR^{11}A$, wherein D can be selected from C_2H_5O and CH_3O ,
3 M is selected from C_2H_5 and CH_3 , R^{11} is a C_2 to C_{20} hydrocarbon chain, x is from 0
4 to 2, and wherein A is an inorganic acid group is selected from $-SO_3H$, -
5 $SO_2NH SO_2CF_3$, $-CF_2SO_3H$, and $-CF_2SO_2NH SO_2CF_3$.
- 1 35. The membrane of claim 27, wherein the first compound including an inorganic acid
2 group is selected from sulfonated phenyltriethoxysilane (SPS), sulfonated
3 phenylethyltriethoxysilane, and 3-(trihydroxysilyl)-1-propane sulfonic acid.
- 1 36. The membrane of claim 27, wherein the Si-O-Si inorganic backbone former
2 compound is selected from tetraethoxysilane and tetramethoxysilane.

1 37. The membrane of claim 27, wherein the membrane includes about 1 to 2 moles of
2 Si derived from the bis(alkylalkoxysilyl)-terminated polymer compound, about 0 to
3 3 moles of Si derived from the bis(trialkoxysilyl)-terminated short organic chain
4 compound, about 0 to 3 moles of Si derived from the first compound including an
5 inorganic acid group, about 0 to 2 moles of Si derived from the Si-O-Si inorganic
6 backbone former compound, and wherein about 10% to 150% of the moles of Si
7 from the bis(alkylalkoxysilyl)-terminated polymer compound, bis(trialkoxysilyl)-
8 terminated short organic chain compound, the first compound including an
9 inorganic acid group, the Si-O-Si inorganic backbone former compound, equals
10 the moles of H_3PO_4 .

1 38. The membrane of claim 28, wherein the membrane includes about 1 to 2 moles of
2 Si derived from the bis(alkylalkoxysilyl)-terminated polymer compound, about 0 to
3 3 moles of Si derived from the bis(trialkoxysilyl)-terminated short organic chain
4 compound, about 0 to 3 moles of Si derived from the first compound including an
5 inorganic acid group, about 0 to 2 moles of Si derived from the Si-O-Si inorganic
6 backbone former compound, about 50% to 100% of the moles of Si from the
7 bis(alkylalkoxysilyl)-terminated polymer compound, bis(trialkoxysilyl)-terminated
8 short organic chain compound, the first compound including an inorganic acid
9 group, the Si-O-Si inorganic backbone former compound, equals the moles of
10 H_3PO_4 , and about 0% to 50% of the moles of H_3PO_4 equals the moles of the
11 heterocycle compound.

1 39. A method of preparing a membrane comprising:

2 providing a sol mixture, wherein the sol mixture is from formed by mixing
3 compounds selected from group 1 or group 2, wherein group 1 comprises at least
4 one hybrid inorganic-organic copolymer network former compound, a first
5 compound including an inorganic acid group, a Si-O-Si inorganic backbone former
6 compound, and a H_3PO_4 compound, and group 2 comprises a bis(alkylalkoxysilyl)-
7 terminated polymer compound, a bis(trialkoxysilyl)-terminated short organic chain
8 compound, a first compound including an inorganic acid group, a Si-O-Si
9 inorganic backbone former compound, and a H_3PO_4 compound;

10 disposing the mixture on a substrate;

11 heating the mixture; and

12 forming a flexible proton electrolyte membrane having the characteristic of
13 a proton conductivity of about 1×10^{-6} to 1×10^{-1} S/cm at a temperature range of
14 about 30°C to about 180°C and a relative humidity of about 0% to 100%.